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INSTITUTE OF ENERGY CONVERSION

UNITED STATES DEPARTMENT OF ENERGY
UNIVERSITY CENTER OF EXCELLENCE
FOR PHOTOVOLTAIC RESEARCH AND EDUCATION

October 3, 2007

Bolko von Roedern
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Re: NREL Subcontract #ADJ-1-30630-12
D.5.18

Dear Bolko,

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period of April 1, 2007 to April 30, 2007 under the subject subcontract. The report highlights progress and results obtained under Task 2 (CIS-based solar cells).

TASK 2: $CuInSe_2$-BASED SOLAR CELLS

$Cu(InGa)(SeS)_2$ Formation by H_2Se/H_2S Reaction

In-Line Evaporation of $Cu(InGa)Se_2$

Roll-to-Roll Deposition of $Cu(InGa)Se_2$ at Different Web Speeds

Experiments have been initiated in the in-line system to determine the effect of web transport speed on the $Cu(InGa)Se_2$ film quality both in terms of the materials characteristics and device performance. The web used as a substrate was 50 µm thick UpilexS polyimide coated with 0.2 µm Mo(O). The baseline web speed has been 0.75"/min, corresponding to an apparent deposition time of 15.2 min for the deposition zone of 11.4".

As a first experiment, a deposition was started at a web speed of 0.75"/min and after 4 ft of deposition the web speed was raised to 1"/min for another 5 ft of deposition. Samples taken at 2' and 7' from the leading edge, corresponding to web speeds of 0.75 and 1"/min were investigated. Table I gives the compositions of the $Cu(InGa)Se_2$ films so sampled. Figure 1 shows the surface topography and cross section of the films taken from the same locations above. The data show that the compositions are similar to within the measurement accuracy as expected.

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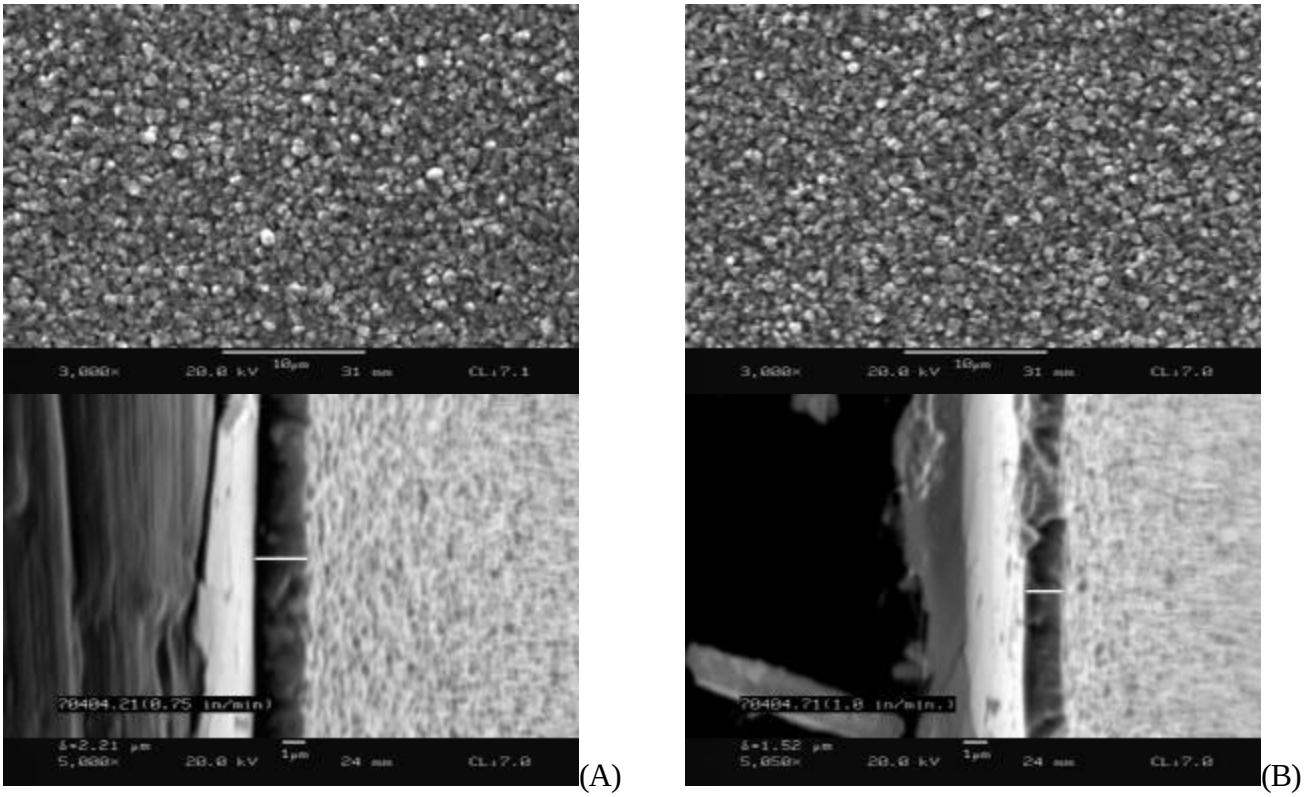
Table I. Composition of the $Cu(InGa)Se_2$ films deposited at 0.75"/min and at 1"/min web speed.

Web Speed (inch/min)	Cu (at%)	Ga (at%)	In (at%)	Se (at%)	Cu/III	Ga/III
0.75	22.6	7.6	19.1	50.7	0.84	0.28
1.00	22.5	8.8	18.6	50.1	0.82	0.32



(A) (B)

Figure 1. Surface topography and cross-section of the $Cu(InGa)Se_2$ films deposited at a web speed of 0.75"/min (A) and 1"/min (B).

On the other hand for the web speed changes of 32%, a variation of 33% is observed in film thickness, which is also what one would expect.

The operational quality of the $Cu(InGa)Se_2$ films from these two locations were evaluated by fabricating devices and comparing their performances. Figure 2 and 3 show the JV data on these devices. The data give a better performance for $Cu(InGa)Se_2$ films grown at 1"/min web speed than the films grown at 0.75"/min. In view of the compositional and structural similarities, this difference is at the present time could not be explained and will be investigated in the future.

70404.21d **Upilex/Mo/CuInGaSe2/CdS/ZnO/ITO/Ni-Al grids**

100 mW/cm2 oriel *Initial test.*

Area: 0.56 *16:09 26-Feb-2007* *Settings: Ron*

Cell	Voc	Jsc	FF	Eff	Roc	Gsc	Vmp	Jmp	Temp	Filename	
001	**0.546**	**25.7**	**28.7**	**4.0**	**11.1**	**25.5**	**0.278**	**14.5**	**24.6**	070226_160903	70404.21d-001.jvtst
001	0.539	28.3	36.9	5.6	9.8	12.5	0.298	18.9	24.9		
002	**0.529**	**26.5**	**31.7**	**4.5**	**8.9**	**21.1**	**0.278**	**16.0**	**24.7**	070226_161217	70404.21d-002.jvtst
002	0.526	28.6	38.3	5.8	9.1	12.6	0.299	19.3	24.8		
003	**0.537**	**26.0**	**30.4**	**4.3**	**10.9**	**23.3**	**0.274**	**15.5**	**24.7**	070226_161538	70404.21d-003.jvtst
003	0.534	28.6	38.2	5.8	9.2	10.4	0.301	19.4	24.9		
004	**0.516**	**26.9**	**32.1**	**4.5**	**10.6**	**22.5**	**0.277**	**16.1**	**24.5**	070226_161859	70404.21d-004.jvtst
004	0.518	29.0	38.0	5.7	8.7	14.5	0.295	19.3	24.7		

average	*0.531*	*27.4*	*34.3*	*5.0*	*9.8*	*17.8*	*0.287*	*17.4*	*24.7*
stdev	*0.01*	*1.215*	*3.71*	*0.727*	*0.89*	*5.5*	*0.011*	*1.89*	*0.13*

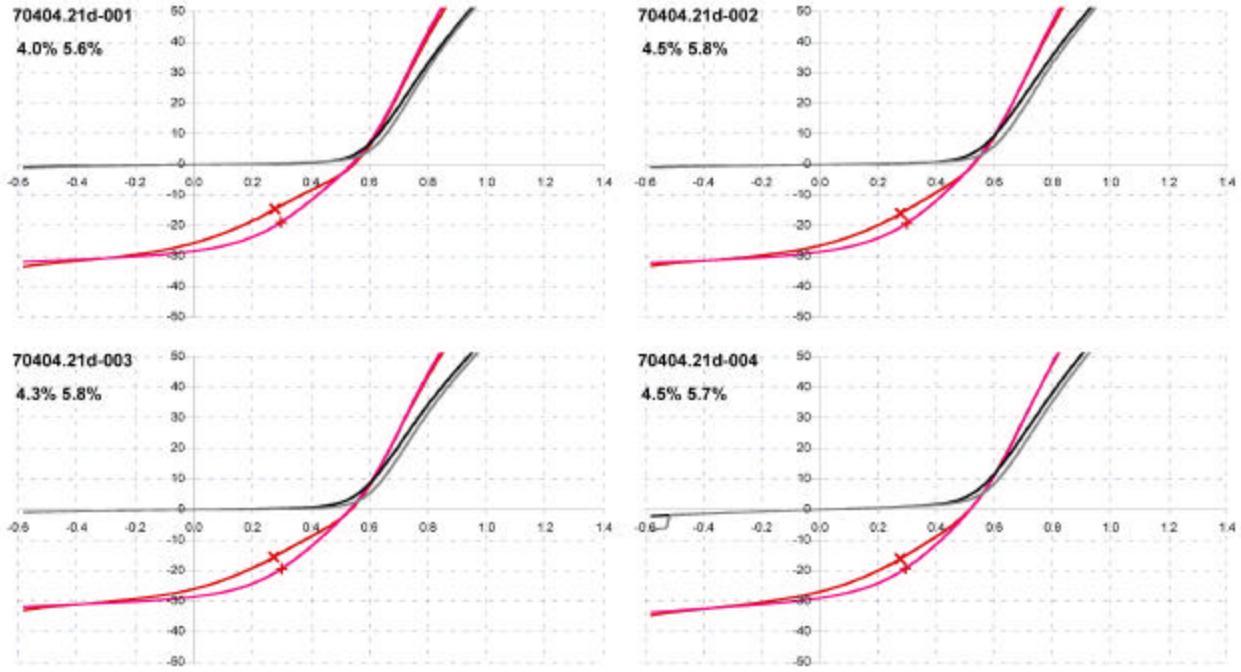


Figure 2. JV characteristics of devices fabricated on Cu(InGa)Se_2 film grown at a web speed of 0.75"/min.

70404.71d **Upilex/Mo/CuInGaSe2/CdS/ZnO/ITO/Ni-Al grids**

100 mW/cm2 oriel *Initial test.*

Area: 0.56 *15:00 27-Feb-2007* *Settings: Ron*

Cell	Voc	Jsc	FF	Eff	Roc	Gsc	Vmp	Jmp	Temp	Filename	
001	**0.532**	**31.8**	**51.9**	**8.8**	**5.5**	**2.5**	**0.348**	**25.3**	**25.2**	070227_150000	70404.71d-001.jvtst
001	0.533	31.7	52.8	8.9	5.3	2.7	0.350	25.4	25.5		
002	**0.529**	**30.3**	**55.3**	**8.9**	**4.7**	**2.5**	**0.364**	**24.3**	**24.9**	070227_151453	70404.71d-002.jvtst
002	0.530	30.3	55.3	8.9	4.6	2.7	0.362	24.5	25.6		
003	**0.530**	**31.1**	**51.7**	**8.5**	**5.5**	**3.6**	**0.348**	**24.5**	**25.1**	070227_151807	70404.71d-003.jvtst
003	0.530	31.2	51.9	8.6	5.4	3.7	0.347	24.7	25.4		
004	**0.532**	**32.3**	**53.8**	**9.2**	**4.4**	**3.2**	**0.363**	**25.4**	**25.3**	070227_152234	70404.71d-004.jvtst
004	0.532	32.4	54.3	9.4	4.4	4.6	0.360	26.0	25.7		

average	*0.531*	*31.4*	*53.4*	*8.9*	*5.0*	*3.2*	*0.355*	*25.0*	*25.3*
stdev	*0.001*	*0.766*	*1.41*	*0.272*	*0.45*	*0.7*	*0.0072*	*0.57*	*0.25*

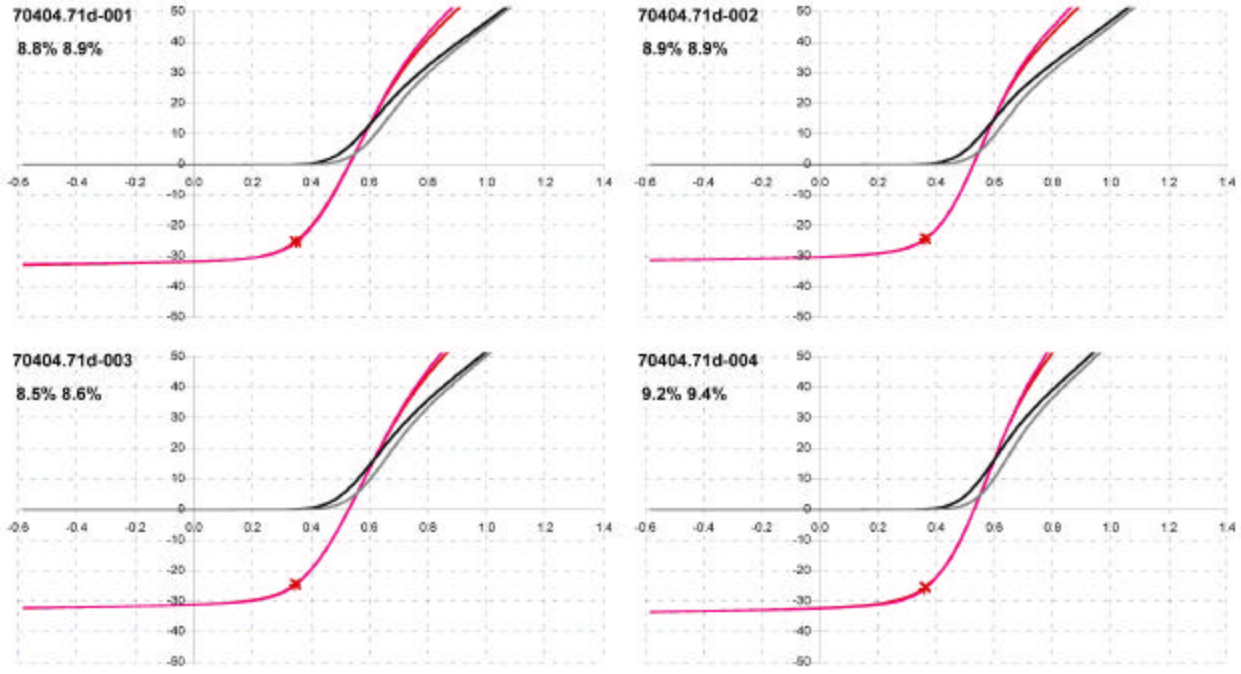


Figure 3. JV characteristics of devices fabricated on Cu(InGa)Se_2 film grown at a web speed of 1"/min.

Improved Performance with Absorber Thickness < 1 µm

The objective in this research task is to develop methods to increase J_{SC} in devices using absorber layers with thickness 0.3 = d = 1.0 µm. One approach is to implement methods of light scattering to improve J_{SC} with thin absorber layers. Experiments to texture ZnO or ITO films are underway and results will be reported next quarter.

A second effort has been to determine if the higher absorption coefficient in $CuInS_2$ 1 or S-containing alloys can be used to increase J_{SC} with thin absorbers. The primary motivation is to determine the extent to which unexplained losses in J_{SC} with absorber layers < 1 μm thick are due to the generation depth as opposed to losses at interfaces or from scattering. $CuInS_2$ films were deposited by a uniform co-evaporation process under Cu-excess conditions with thicknesses 1.9, 0.9, and 0.5 μm. Figure 4 shows SEM images of the as-deposited films which shows the grain size decreases with changes with the film thickness

The films were etched in a 0.5 M KCN aqueous solution to remove Cu_xS_y prior to the CdS layer deposition and solar cells with SL glass/Mo/CIGSS/CdS/ZnO/ITO/Ni-Al structure were fabricated. The J-V parameters of the cells are listed in Table II and QE curves shown in Figure 5. Figures 4(a) and 4(b) show external QE and normalized internal QE, respectively. For comparison, the calculated spectral response from absorption coefficient[1] for each thickness absorber is shown in Fig. 4(c). Compared with the calculated QE curves, the decrease in QE in the range 600 – 800 nm with thickness is greater than expected. This decrease may be caused by the decreasing grain size with film thickness.[2,3]

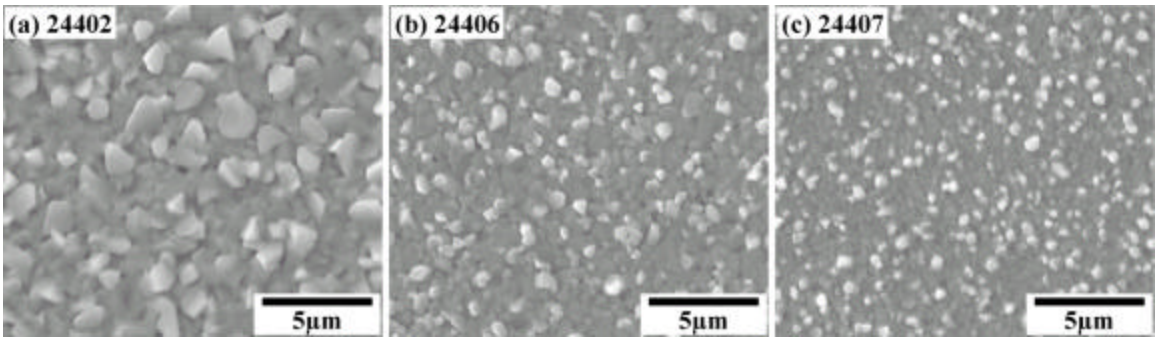


Figure 4. Microstructure change with film thickness.

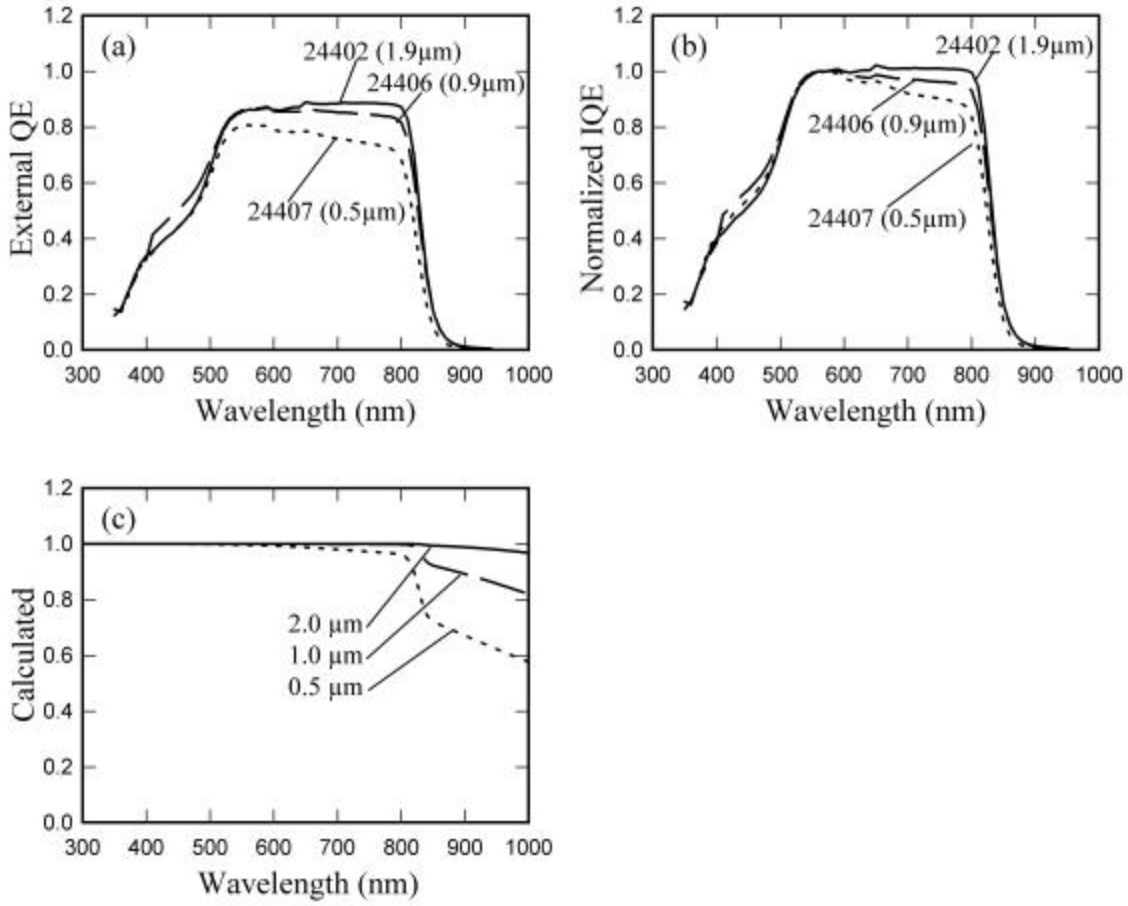


Figure 5. Spectral response depending on the absorber thickness. (a) external QE, (b) normalized internal QE, and (c) calculated from absorption coefficient of $CuInS_2$.

Table II. Solar cell properties.

Sample	thickness (μm)	Eff. (%)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)
24402	1.9	8.22	0.619	22.07	60.0
24406	0.9	7.41	0.608	20.81	58.4
24407	0.5	5.39	0.553	19.79	49.1

$Cu(InGa)(SeS)_2$ Formation by Reaction in H_2Se/H_2S

In this task, the objective is to develop methods for controlling through-film composition in the formation of $Cu(InGa)(SeS)_2$ films by the reaction of metal precursors to enable formation of devices with increased V_{OC}. Previously, IEC has developed and characterized a baseline process consisting of a 15 minute reaction in 0.35% H_2Se/0.0035% O_2 at 450 ºC followed by either 15 or 30 minute reaction in 0.35% H_2S/0.0035% O_2 at 550 ºC4. This process results in $Cu(InGa)(SeS)_2$ films with uniform Ga composition and high S concentration near the film

surface. Devices fabricated on these absorber layers have achieved efficiencies in excess of 13% with V_{OC} = 0.64 V.

In addition to previously presented XRD, SEM, EDS, and Auger characterization of baseline IEC films, cross-sectional SEM images are shown in Figure 6 for $Cu(InGa)Se_2$ and $Cu(InGa)(SeS)_2$ films formed by precursor reaction. These images were provided by Bobby To at NREL. The $Cu(InGa)Se_2$ film, reacted at 450°C for 60 min to fully consume intermetallic phases, has small grains and periodic voids at the back of the film. The $Cu(InGa)(SeS)_2$ film reacted in H_2Se for 15 min at 450°C, then H_2S for 15 min at 550°C has much larger grains but still has the voids. The increase in grain size results from the reaction at higher temperature with H_2S but the relative importance of the thermal and chemical effects are not yet know. The voids are consistent with previous IEC observations of the backsides of delaminated $Cu(InGa)(SeS)_2$ films.

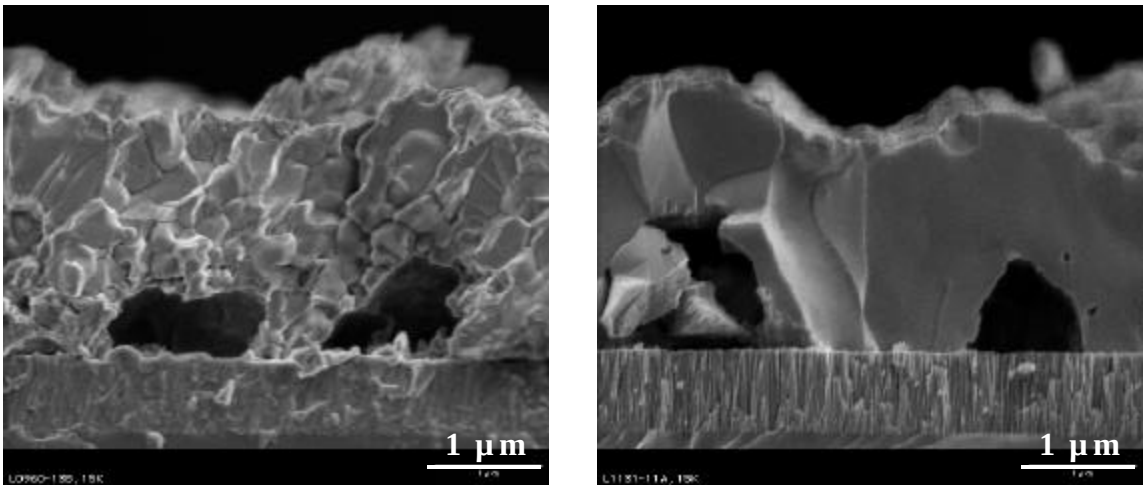


Figure 6. Cross-sectional SEM images of reacted $Cu(InGa)Se_2$ (left) and $Cu(InGa)(SeS)_2$ (right) films.

To more fully comprehend the Ga homogenization that occurs during the sulfization process, a series of experiments are being undertaken in which the sulfization temperature is being varied from 450 to 550ºC. Of interest are the reaction rate of the Cu_9Ga_4 intermetallic present after the selenization step, the Ga homogenization mechanism, and the device performance.

Figure 7 shows residual Cu_9Ga_4 intermetallics on the Mo back contact after delamination of a $Cu(InGa)(SeS)_2$ film that was selenized for 15 min at 450 ºC in H_2Se, followed by a 15 minute sulfization at a reduced temperature of 450ºC. The presence of the Cu_9Ga_4 intermetallics was verified by EDS and XRD measurements. This differed from the previous IEC results in which the intermetallics were completely reacted in the baseline process with the 15 min H_2Se reaction at 550°C and also the complete reaction of Ga from intermetallic precursors in H_2S at 450ºC in only 10 minutes.[4] The overlying chalcopyrite film is apparently acting as a diffusion barrier at these reduced temperatures, slowing the delivery of S to the Cu_9Ga_4 intermetallic.

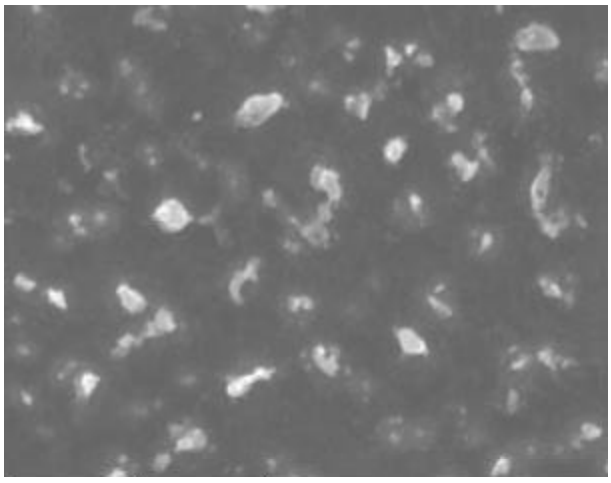


Figure 7. Residual Cu_9Ga_4 intermetallics on Mo back contact after delamination of $Cu(InGa)(SeS)_2$ formed by 15 min selenization at 450ºC followed by a 15 minute sulfization at a reduced temperature of 450 ºC.

Not unexpectedly, given the observation of unreacted Cu_9Ga_4 intermetallics at the back contact after sulfization at 450ºC, XRD and EDS measurements indicated negligible Ga incorporation into the overlying $Cu(InGa)(SeS)_2$ film. The peak maximum of the $Cu(InGa)(SeS)_2$ 112 peak possessed a d-spacing of 3.334, where as a baseline $Cu(InGa)(SeS)_2$ film would possess a d-spacing of approximately 3.300 Å, and pure component $CuInSe_2$ possesses a d-spacing of 3.351 Å. The EDS measurements with 20kV electrons gave 24.5% Cu, 24.6% In, 1.1% Ga, 46.0% Se and 3.5% S. This yields composition ratios of Ga/(In+Ga) = 0.04 and S/(Se+S) =0.07 . The ratios in the baseline $Cu(InGa)(SeS)_2$ film with H_2S reaction at 550°C are Ga/(In+Ga) = 0.18 and $0.20 < S/(Se+S) < 0.30$.

Additional results with intermediate temperatures and device results will be reported in the next quarter.

Best regards,

Robert W. Birkmire
Director

RWB/eak

Cc: Paula Newton, IEC
Susan Tompkins, RGS
Carolyn Lopez, NREL

References

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